

## **Cd(II) ADSORPTION FROM AQUEOUS SOLUTION BY ACTIVATED CARBON FROM SUGAR BEET PULP IMPREGNATED WITH PHOSPHORIC ACID**

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## SUMMARY

The adsorption of Cd(II) ions from aqueous solutions onto activated carbon obtained by carbonising sugar beet pulp impregnated with 30% phosphoric acid was studied. By increasing the temperature of carbonisation, the removal efficiency of Cd(II) ions increased. The maximum removal (95.8%) was attained by activated carbon samples obtained by carbonising acid-impregnated sugar beet pulp at 500 °C for 90 min. The removal efficiency of Cd(II) ions is, to a large extent, dependent on pH of medium. The results of experiments carried out at various temperatures were applied to Langmuir and Freundlich isotherm equations. The values of Langmuir constant ( $q_{\max}$ ) at 20 °C were calculated as 68.03, 71.99 and 72.99 mg/g for activated carbons obtained at 300, 400 and 500 °C, respectively. The adsorption process was found to be exothermic and Langmuir isotherm data were evaluated to determine the thermodynamic parameters for the adsorption process. It was found that the values of  $q_{\max}$  and  $K_f$  decreased with increasing temperature. The data are better fitted by the second-order kinetic model as compared to first-order kinetic model.

**KEYWORDS:** Sugar beet pulp, Activated carbon, Cd(II) ions removal, Phosphoric acid.

## INTRODUCTION

There are various pollutants released to the aquatic environment from wastes produced as a result of many industrial activities playing an important role in the technological development. The most important groups of these pollutants are heavy metals that do not degrade into harmless end-products by natural physiological mechanisms, but accumulate in the living bodies by the food chain, especially during the use of surface water [1].

Cadmium is generally considered to be one of the most toxic metals found in the environment. Mining and metallurgy of cadmium, cadmium electroplating, battery and accumulator manufacturing, pigments, ceramics, textile printing industry wastewaters and lead mine drainage [2, 3], but also sewage sludge [4] contain various amounts of Cd(II) ions. The main treatment processes for the removal of Cd(II) ions from waste streams include its precipitation as hydroxide [2, 5] and carbonate [6], evaporation, adsorption, ion exchange, membrane processing, solvent extraction etc. [3]. Adsorption and ion exchange processes have significant benefits –the treated water is often sufficiently pure to be recycled and re-used, and adsorbed metals can be often recovered and purified in well designed regeneration processes [7]. Activated carbon is the most widely studied adsorbent for the removal of Cd(II) ions from aqueous solution. Since activated carbon production is too expensive for large-scale use, various alternative sources have been used in its production. Therefore many studies have been focused on preparation of activated carbons from cheaper and readily available materials such as coirpith [8], coconut tree sawdust [9], almond shells, olive and peach stones [10], oil palm stones [11] and plum kernels [12]. On the other hand some cellulosic materials such as coconut shell and raw rice husk [13], water hyacinth [14], nut and walnut shells, waste tea [15], pine bark [16], pinus pinaster bark [17] and biosorbents [18-20] have been used in the adsorption of Cd(II) ions from aqueous solutions. But, activated carbon adsorption appears to be a particularly competitive and effective process for the removal of Cd(II) ions and other toxic metals at trace quantities. In this context, we have studied Cd(II) ion adsorption by activated carbon prepared from sugar beet pulp, which is an abundant and cheap material produced in sugar industry as a by-product.

The objective of the present study was to investigate the effects of carbonisation temperature, contact time, initial pH and contact temperature on the adsorption of

Cd(II) ions by activated carbon prepared from sugar beet pulp impregnated with phosphoric acid. Equilibrium isotherm data were well fitted to Langmuir and Freundlich isotherm equations and the isotherm constants were determined. Also, adsorption kinetics of Cd(II) ions were analysed by applying the pseudo first-order and pseudo second-order kinetic models to the data.

## MATERIALS AND METHODS

### Material

Sugar beet pulp was provided from a local sugar factory in Elazığ, Turkey. The conversion of sugar beet pulp to activated carbon was carried out as following:

Raw sugar beet pulp was dried on a polyethylene layer and stored in a closed jar. A sample of 50 g of dried sugar beet pulp was treated with 200 ml phosphoric acid (30 %) for 24 hours. The phosphoric acid-treated biomass was then filtered by suction, washed with 500 ml distilled water to remove excess acid from sugar beet pulp and dried to minimize humidity. The carbonisation process was carried out by heating the phosphoric acid-treated samples in a fixed bed at different temperatures (300, 400 and 500 °C) in a constant flow rate of N<sub>2</sub> for 90 min. Since the activated carbon samples had a jelly structure, they were washed with deionised water to remove the excess phosphoric acid and filtered until the pH of the supernatants remained constantly at around 4.0. The activated carbons were dried at 105 °C, ground and sieved to obtain the 100 mesh fraction. This fraction was stored in desiccators filled with CaCl<sub>2</sub> during the experimental study.

The BET surface area of activated carbons was determined by N<sub>2</sub> gas adsorption technique using a Quantachrome Monosorb Direct Surface Analyser apparatus. The iodine number (IN) of activated carbons was determined by shaking 0.5 g of each sample with 100 ml aqueous solution of iodine (2.7 g I<sub>2</sub> /l) at 25 °C. After a shaking period of 45 min, the suspension was filtered and the concentration of residual iodine was determined by titrating the supernatant with 0.1 N sodium thiosulphate solution. The gram amount of iodine adsorbed per gram carbon was taken as iodine number. Fixed carbon and acid-insoluble matter contents of the activated carbons were determined by the method described in [21].

### Preparation of solutions

Working solutions of Cd(II) ions were prepared by diluting a 1000 mg/l stock Cd(II) solution which was obtained by dissolving analytical grade cadmium sulphate (3CdSO<sub>4</sub>·8H<sub>2</sub>O) supplied by Reidel-de Haen Chemicals. Other reagents used in this study were of analytical grade. The pH of each solution was adjusted to the required value by using 0.1 M NaOH or 0.1 M HCl solution. All dilutions and solutions were made by using distilled water.

### Adsorption Experiments

Adsorption experiments were carried out by shaking 50 ml of a 100 mg/l Cd(II) solution with 0.25 g of activated carbon obtained at different temperatures in 100 ml flasks with contact times ranging from 5 to 240 min. The flasks were shaken at constant rate using a flask shaker (Clifton) with thermostatic water bath. To obtain different initial pH values for each working solution, 5 ml stock Cd(II) solution was added to a 50 ml glass bottle and diluted up to the mark with deionised water and NaOH or HCl solution.

For isotherm studies, a series of flasks containing 50 ml Cd(II) solution in the range of 50-500 mg/l were prepared. 0.25 g activated carbon was added to each vial and the mixtures were agitated at constant temperature. These experiments were carried out at constant pH 6.3 for a contact period of 60 min.

At the end of the contact period required, the aqueous phase was separated from activated carbon by centrifugation at 5000 rpm for 10 min and the concentration of residual Cd(II) ions in the supernatants was determined by atomic absorption spectrophotometry (Perkin Elmer 370 model). The amount of adsorbed Cd(II) ions was calculated by the difference of initial and final concentration.

All experiments, except for isotherm studies, were conducted at 20 °C in duplicate and average values were reported.

## RESULT AND DISCUSSIONS

### Characterisation of activated carbons

Some properties of activated carbons used in this study are presented in Table 1. The yield of activated carbons decreases depending on the rise in temperature of carbonisation. The removal efficiency of volatile substances from phosphoric acid-impregnated sugar beet pulp depends, to a large extent, on the carbonisation temperature, which causes a decrease in fraction of fixed carbon in carbonisation products. It can be seen that BET surface areas of activated carbons do not show a regular change with carbonisation temperature. The value of BET surface area of activated carbon obtained at 400 °C is higher than those of other activated carbons. The lower value of surface area of activated carbon produced at 500 °C may be attributed to the conversion of micropores to mesopores or macropores, resulting in lower surface area. On the other hand, the iodine number increased from 356.0 to 449.4 mg/g when carbonisation temperature increased from 300 °C to 500 °C. It is clear that there is no regular relation between the iodine adsorption capacities of activated carbons and their surface area. The adsorption of iodine molecules by activated carbon may be expressed in two ways; the binding of iodine molecules on the active sites by chemical bonds and the physical adsorption of

TABLE 1  
Some characteristics of activated carbons from sugar beet pulp impregnated with phosphoric acid.

| Carbonisation temp. (°C) | Yield (%) | BET surface area (m <sup>2</sup> /g) | Iodine number (mg I <sub>2</sub> /g) | Carbon content (%) | Acid-insoluble matter (%) |
|--------------------------|-----------|--------------------------------------|--------------------------------------|--------------------|---------------------------|
| 300                      | 33.8      | 187.9                                | 356.0                                | 86.0               | 6.0                       |
| 400                      | 31.0      | 328.8                                | 387.9                                | 77.0               | 6.9                       |
| 500                      | 28.0      | 199.0                                | 449.4                                | 72.4               | 8.2                       |

these molecules in the pores. It is probably that at lower temperatures the number of active sites is not sufficient to uptake the iodine molecules chemically. In this case, a rise in carbonisation temperature may lead to an enhance in the number of active sites and increases the adsorption yield of iodine molecules. Although it is expected that the carbon content of activated carbons increases with increasing carbonisation temperature, an opposite behaviour was observed. This situation is caused by oxygen. Oxygen is present as impurity in nitrogen gas passing over sugar beet pulp during the carbonisation procedure. This causes a decrease in carbon content of carbonised materials as a result of C-O<sub>2</sub> reaction efficiently taking place at higher temperatures. In addition, oxygen in compounds may contribute to this carbon loss by a decarboxylation. The amounts of acid-insoluble matters, which is a measure of undissolved inorganic compounds such as metal oxides and silicates, were determined as 6.0%, 6.9% and 8.2 % for activated carbons obtained at 300 °C, 400 °C and 500 °C, respectively. These compounds form the ash content of activated carbons. The fraction of inorganic compounds increased relatively with increasing carbonisation temperature, while the amount of carbon in the resulting products decreased at higher temperature.

#### Cadmium adsorption

##### Effect of initial pH

The solution pH affects the surface charge of adsorbent, the degree of ionisation and the speciation of the surface function groups [22]. For that reason, in many studies carried out to remove heavy metals from aqueous solutions, it has been pointed out that the solution pH is one of the most important parameters affecting adsorption yield. The effect of initial pH on the adsorption of Cd(II) ions was studied by contacting 0.25 g activated carbon from sugar beet pulp with 50 ml Cd(II) solution (100 mg/l) for 60 min at 20 °C. The initial pHs of the working solutions are varied from 2.0 to 11.8. The results of these experiments are given in Fig. 1. The removal percentage of Cd(II) ions increased sharply with pH values up to 6.3, and after pH 9.0 it tended to decrease, as is evident in Fig.1. The maximum removal percentages were found to be 90.6 %, 93.4 % and 95.8 % at initial pH 6.3 for activated carbons obtained at 300, 400 and 500 °C, respectively. As can be seen from Fig.1 the adsorption yield is very low in strongly acidic medium. This has already

been noticed by several workers [23-25]. The lower adsorption percentage observed at low pHs may be explained on the basis of electrostatic repulsion forces between positively charged H<sub>3</sub>O<sup>+</sup> and Cd<sup>2+</sup> ions. At low pH values, the concentration of H<sub>3</sub>O<sup>+</sup> is higher than that of Cd(II) ions and, hence, these ions are adsorbed on the active sites of activated carbons, leaving Cd(II) ions free in the solution. When the pH increased, Cd(II) ions would replace H<sub>3</sub>O<sup>+</sup> ions because of competing effects, which increased the adsorption yield of the Cd(II) ions.

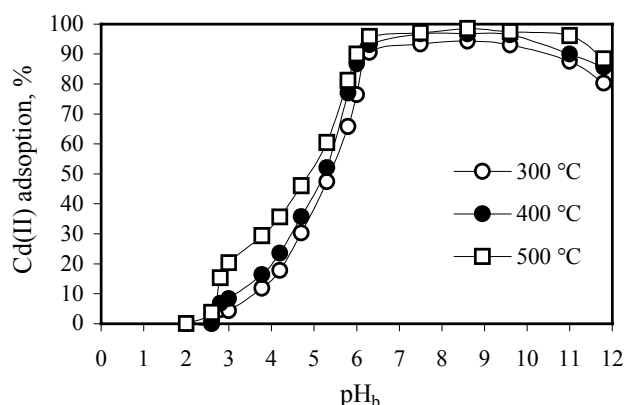
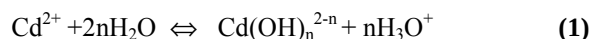


FIGURE 1 - Effect of initial pH on the adsorption of Cd(II) ions by activated carbons from sugar beet pulp (Conditions: 50 ml of 100 mg/l Cd(II) solution; 0.25 g activated carbon obtained at different temperatures; contact time 60 min.; contact temperature 20 °C).

The hydrolysis and precipitation of metal ions affect adsorption by changing the concentration and forming of soluble metal species available for adsorption. The hydrolysis of Cd(II) ions may be represented by the following reaction:



As suggested by Reed and Matsumoto [26], various species of cadmium can be formed as a function of pH (Fig. 2). The hydrolysis extend of Cd(II) ions is not important up to approximately pH 7.5. It can be clearly seen that the concentration of Cd(OH)<sup>+</sup> ions reaches a maximum at around pH 9.5. At pH values > 8.0 the removal takes place by adsorption as well as precipitation of Cd(II) ions in the form of Cd(OH)<sub>2</sub>. Precipitation of Cd(II) ions begins theoretically at pH values of 8.3 for the

concentration of 100 mg/l. Therefore optimum pH for Cd(II) ions adsorption was selected as 6.3. At this pH value the adsorption of Cd(II) ions was not masked by precipitation. The optimum pH for Cd(II) ions adsorption from aqueous solutions by activated carbons from almond shells, olive and peach stone has been reported as 5.0 [10]. In other studies carried out with activated carbon from coirpith, maximum removal was attained at pH 4.0 [8]. Optimum pH for adsorption of Cd(II) ions by activated carbon from bagasse was reported as 4.5 [25]. Cimino et al. [27] have reported that maximum removal in the adsorption of Cd(II) ions by carbon from hazelnut shell treated with sulphuric acid was observed in the pH range from 4.0 to 6.0. In our previous study [24] related to Cd(II) ions adsorption, optimum pH has been found to be 6.3. In another study using Girdih coal to remove Cd(II) ions from aqueous solutions, the maximum removal percentage was observed at pH 6.6 [13]. These results show that the adsorption yield of Cd(II) ions by various adsorbents is dependent on pH of solution. The decrease in adsorption yield at pH > 9.0 can be attributed to the formation of  $\text{Cd}(\text{OH})_3^-$  ions taking place as a result of dissolution of  $\text{Cd}(\text{OH})_2$ , due to its amphoteric characteristic. Since cadmium is present in the form of  $\text{Cd}^{2+}$  ions at optimum pH 6.3, the adsorption mechanisms can be explained on the basis  $\text{H}_3\text{O}^+ - \text{Cd}^{2+}$  exchange reaction which was a function of solution pH.

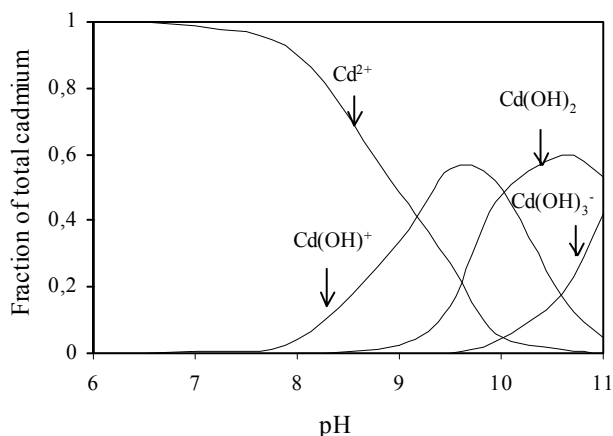


FIGURE 2  
Speciation of Cd(II) as a function of pH.

#### Effect of contact time

The influence of contact time on the removal of Cd(II) ions by activated carbon samples produced at different temperatures is illustrated in Fig. 3. The removal percentage of Cd(II) ions by activated carbons increased with increasing contact time and attained an equilibrium after 60 min for the initial concentration of 100 mg/l. Although the adsorption yield of activated carbon obtained at 500 °C is higher than that of the other experiments, there is no remarkable difference among their adsorption yields. It can be seen that the majority of Cd(II) ions is adsorbed within the first 5 min. For this

time, 60.0 %, 66.0 % and 70.7 % of total Cd(II) ions were removed from the solution by activated carbons obtained at 300, 400 and 500 °C, respectively. After equilibration time, it was observed that there was only a small increase in the removal yield by increasing the contact time.

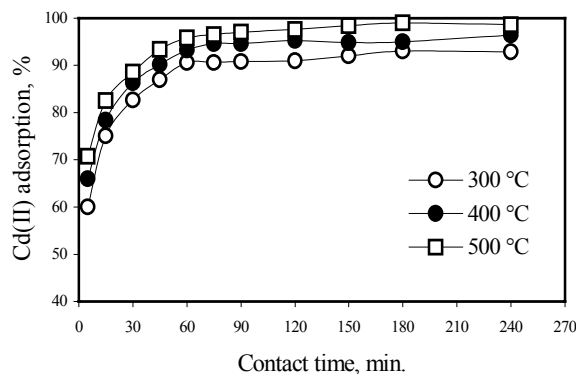


FIGURE 3 - Effect of contact time on the adsorption of Cd(II) ions by activated carbons from sugar beet pulp (Conditions: 50 ml of 100 mg/l Cd(II) solution; 0.25 g activated carbon obtained at different temperatures; initial pH 6.3; contact temperature 20 °C).

The equilibrium times for the adsorption of Cd(II) ions on the different adsorbents have been reported in a wide range of contact time. The parameters such as stirring rate of suspension, physical and chemical properties of adsorbent (porosity, surface area, the structure of functional groups, active adsorption sites), and adsorbate (atomic and ionic radius, polarity and electronic charge) have an important influence on the equilibrium time. The equilibrium times required for the removal of Cd(II) ions by activated carbons from sugar beet pulp are quite low, which can be evaluated as an advantage from the point of view of process economy.

#### Adsorption isotherms and thermodynamic parameters

In equilibration experiments, a fixed amount of activated carbons (0.25 g) and 50 ml Cd(II) solution with various concentrations (50-500 mg/l) was placed in a 100 ml glass stoppered flask and shaken in a thermostatic shaker bath for 60 min at constant pH. The equilibrium between adsorbed Cd(II) ions on the activated carbons and Cd(II) ions remaining in solution was described by using Langmuir and Freundlich models. The linear form of Langmuir isotherm can be written as

$$\frac{C_e}{q_e} = \frac{1}{K q_{\max}} + \frac{C_e}{q_{\max}} \quad (2)$$

where  $C_e$  is the equilibrium concentration of the adsorbate (mg/g),  $q_e$  is the amount adsorbed per unit mass of adsorbent (mg/g),  $q_{\max}$  is the maximum adsorption capacity (mg/g),  $K$  (l/mg) is a constant related to the affinity of binding sites or bonding energy and  $q_{\max}$  represents a practical limiting adsorption capacity when the surface of adsorbent is completely covered with adsorbate.

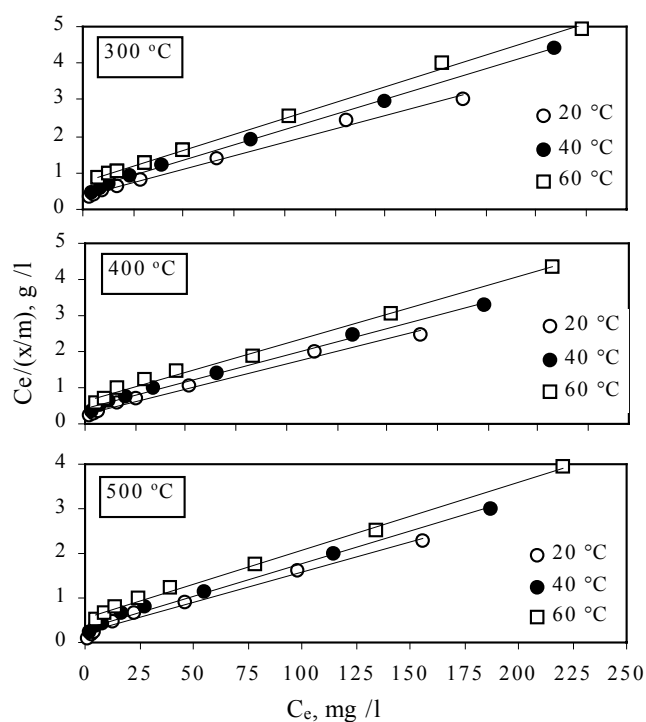


FIGURE 4 - Langmuir plot of Cd(II) ions adsorption by activated carbons from sugar beet pulp (Conditions: contact time 60 min., 0.25 g activated carbon obtained at different temperatures; initial pH 6.3).

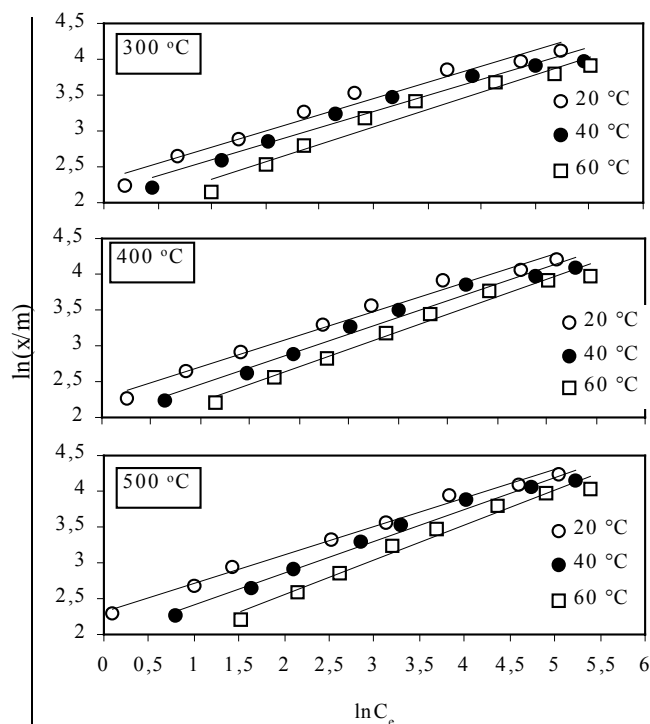


FIGURE 5 - Freundlich plot of Cd(II) ions adsorption by activated carbons from sugar beet pulp (Conditions: contact time 60 min., 0.25 g activated carbon obtained at different temperatures; initial pH 6.3).

TABLE 2 - Langmuir isotherm constants for adsorption of Cd(II) ions on activated carbon from sugar beet pulp impregnated with phosphoric acid.

| Carbonisation temp. (°C) | Isotherm temp. (°C) | Langmuir constants |          |       |
|--------------------------|---------------------|--------------------|----------|-------|
|                          |                     | $q_{\max}$ (mg/g)  | K (l/mg) | $R^2$ |
| 300                      | 20                  | 68.03              | 0.039    | 0.993 |
|                          | 40                  | 59.52              | 0.034    | 0.999 |
|                          | 60                  | 57.80              | 0.022    | 0.997 |
| 400                      | 20                  | 71.99              | 0.047    | 0.989 |
|                          | 40                  | 67.57              | 0.034    | 0.994 |
|                          | 60                  | 62.89              | 0.025    | 0.995 |
| 500                      | 20                  | 79.99              | 0.064    | 0.987 |
|                          | 40                  | 68.97              | 0.045    | 0.996 |
|                          | 60                  | 65.36              | 0.028    | 0.997 |

TABLE 3 - Freundlich isotherm constants for adsorption of Cd(II) ions on activated carbon from sugar beet pulp impregnated with phosphoric acid.

| Carbonisation temp. (°C) | Isotherm temp. (°C) | Freundlich constants |       |       |
|--------------------------|---------------------|----------------------|-------|-------|
|                          |                     | $K_f$                | n     | $R^2$ |
| 300                      | 20                  | 6.449                | 2.202 | 0.970 |
|                          | 40                  | 5.481                | 2.236 | 0.969 |
|                          | 60                  | 3.851                | 2.047 | 0.962 |
| 400                      | 20                  | 7.734                | 2.275 | 0.983 |
|                          | 40                  | 5.817                | 2.146 | 0.979 |
|                          | 60                  | 4.385                | 2.052 | 0.979 |
| 500                      | 20                  | 10.039               | 2.520 | 0.992 |
|                          | 40                  | 7.201                | 2.260 | 0.980 |
|                          | 60                  | 4.779                | 2.045 | 0.977 |

Hence, a plot of  $C_e/q_e$  vs.  $C_e$  should be a straight line with a slope  $1/q_{\max}$  and intercepts  $1/Kq_{\max}$  (Fig. 4), indicating that the adsorption of Cd(II) ions on the activated carbons from sugar beet pulp follows the Langmuir models. The parameters related for the fitting to Langmuir equation at different temperatures for three activated carbon samples are summarized in Table 2.

The equilibrium data for Cd(II) ions also fitted to Freundlich model. This model deals with multilayer adsorption of the substances on the adsorbents. The logarithmic form of this model is given by the following equation:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (3)$$

where  $K_f$  and  $n$  are the Freundlich constants. The values of  $K_f$  and  $n$  may be calculated from the slopes and intercepts of the lines by plotting  $\ln q_e$  against  $\ln C_e$ , as depicted in Fig. 5. The calculated values of  $K_f$  and  $n$  for activated carbons obtained at 300, 400 and 500 °C are presented in Table 3.

The values of regression coefficients ( $r^2$ ) in Tables 2 and 3 showed that Langmuir and Freundlich models adequately described the equilibrium data, but the data fitted better to Langmuir isotherm than to that of Freundlich for adsorption of Cd(II) ions on activated carbon samples. The maximum adsorption capacities ( $q_{\max}$ ) decreased from 68.03 to 57.80, 71.99 to 62.89 and 72.99 to 65.36 mg/g with rise in temperature from 20 to 60 °C for Cd(II) ions uptake on activated carbons obtained at 300, 400 and 500 °C, respectively. While the values of  $q_{\max}$  and  $K$  increase with a rise in carbonisation temperature, their values also exhibit a decreasing trend depending on the isotherm temperature.

Although various kinds of adsorbents are used to remove Cd(II) ions, the results obtained in these studies reveal major differences in their adsorption capacities. For adsorption of Cd(II) ions by activated carbon derived from bagasse, Mohan and Singh [25] found  $q_{\max}$  value as 38.08 mg/g and maximum Cd(II) uptake by carbon from hazelnut shell was 5.42 mg/g [27]. In a study carried out with sugar beet pulp, the maximum adsorption capacity has been found to be 24.39 mg/g for Cd(II) ions adsorption [22]. The maximum cadmium adsorption capacity was 2.5 mg/g for almond shell carbon, 5.91 mg/g for olive stone carbon, 3.27 mg/g for peach stone carbon [10], 7.87 mg/g for granulated activated carbon [28], 12.01 mg/g for apricot stone carbon, 11.1 mg/g for coconut shell carbon, 9.8 mg/g for lignite coal carbon [29] and 3.37 mg/g for granular and powdered activated carbons [30]. The adsorption capacity ( $q_{\max}$ ) of activated carbons used in the present study was higher than those of the adsorbents mentioned above. It must be noted that the direct comparison of removal capacities of activated carbons from sugar beet pulp with those of other adsorbents is difficult due to different experimental conditions applied in the studies cited.

The values of  $K_f$  (at 20°C), assumed as measure of adsorption capacity, increased from 6.449 to 10.039 with

increasing carbonisation temperature from 300 to 500 °C. On the other hand, the values of  $K_f$  decreased with increase of the temperature at which the isotherms were constructed (Table 3). As can be seen from this table, the values of  $n$  are higher than 1, indicating that the Cd(II) ions are favourably adsorbed by the activated carbons at all the temperatures studied. The situation  $n > 1$  is most common and may be due to a distribution of surface sites or any factors that cause a decrease in adsorbent-adsorbate interaction with increasing surface density [26]. The values of  $n$  in the range of 2-10 represent good adsorption [31].

Changes of thermodynamic parameters, such as enthalpy ( $\Delta H^\circ$ ), free energy ( $\Delta G^\circ$ ) and entropy ( $\Delta S^\circ$ ), were also calculated using equations (4), (5) and (6).

$$\ln K = \ln K' - \frac{\Delta H^\circ}{R} \left( \frac{1}{T} \right) \quad (4)$$

$$\ln \left( \frac{1}{K} \right) = \frac{\Delta G^\circ}{R} \left( \frac{1}{T} \right) \quad (5)$$

$$\Delta S^\circ = \frac{(\Delta H^\circ - \Delta G^\circ)}{T} \quad (6)$$

The enthalpy changes of the process determined from the slope of the line obtained by plotting  $\ln K$  vs.  $1/T$  (Fig. 6) were found to be -11.48, -13.14 and -16.57 kJ/mol for the activated carbons prepared at 300, 400 and 500 °C, respectively. The negative values of  $\Delta H^\circ$  confirm the exothermic nature of the process for all three activated carbons. The values of other thermodynamic parameters are given in Table 4. The negative values of  $\Delta G^\circ$  at different temperatures are due to the fact that the process is spontaneous with high preference of Cd(II) ions for activated carbon samples. The free energy change increases with increasing temperature showing that the adsorption feasibility decreases at higher temperatures. The entropy change for the adsorption process has a positive sign, which reflects the affinity of activated carbons for Cd(II) ions in the solution.

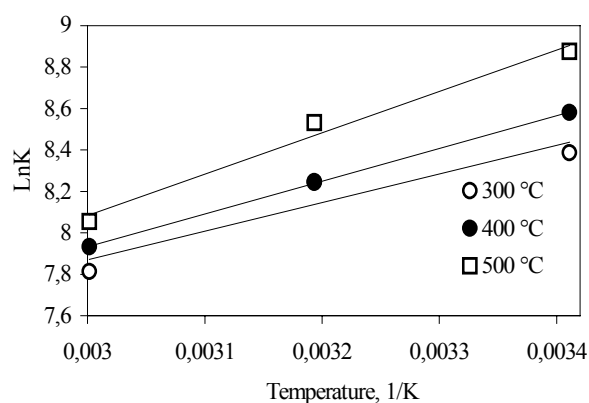


FIGURE 6 - Plot of  $\ln K$  vs.  $1/T$  for the enthalpy change of the adsorption process.

**TABLE 4 - Thermodynamic parameters for the adsorption of Cd(II) ions on activated carbons from sugar beet pulp impregnated with phosphoric acid.**

| Temp.<br>(°C) | Carbonisation temperature (°C) |                   |                  |                   |                  |                   |
|---------------|--------------------------------|-------------------|------------------|-------------------|------------------|-------------------|
|               | 300                            |                   | 400              |                   | 500              |                   |
|               | -ΔG°<br>(kJ/mol)               | ΔS°<br>(kJ/mol K) | -ΔG°<br>(kJ/mol) | ΔS°<br>(kJ/mol K) | -ΔG°<br>(kJ/mol) | ΔS°<br>(kJ/mol K) |
| 20            | 20.44                          | 0.109             | 22.34            | 0.113             | 24.58            | 0.123             |
| 40            | 20.10                          | 0.108             | 21.46            | 0.110             | 23.63            | 0.121             |
| 60            | 19.04                          | 0.104             | 21.65            | 0.108             | 22.31            | 0.117             |

**Adsorption kinetics**

In order to determine the adsorption rate constant, pseudo-first order and pseudo-second order kinetic models were applied to the experimental data. The first order kinetic model known as Lagergren rate equation was the first rate equation for the adsorption of liquid/solid systems based on the solid capacity [32], and is generally expressed as follows:

$$\frac{dq_t}{dt} = k_{1,ad}(q_e - q_t) \quad (7)$$

The pseudo second-order model is also based on the adsorption capacity of a liquid/solid system. If the rate of adsorption is a second-order mechanism, the kinetic rate equation can be written as follows:

$$\frac{dq_t}{dt} = k_{2,ad}(q_e - q_t)^2 \quad (8)$$

where  $q_e$  (mg/g) is the amount of adsorbate at equilibrium,  $q_t$  is the amount of adsorbate at any time  $t$ ,  $k_{1,ad}$  (l/min) and  $k_{2,ad}$  (g/mg min) are the rate constants of pseudo first-order and pseudo second-order adsorption, respectively. Integrating of the equation 7 for the boundary conditions  $t=0$  to  $t=t$  and  $q_t=0$  to  $q_t=q_t$ , gives:

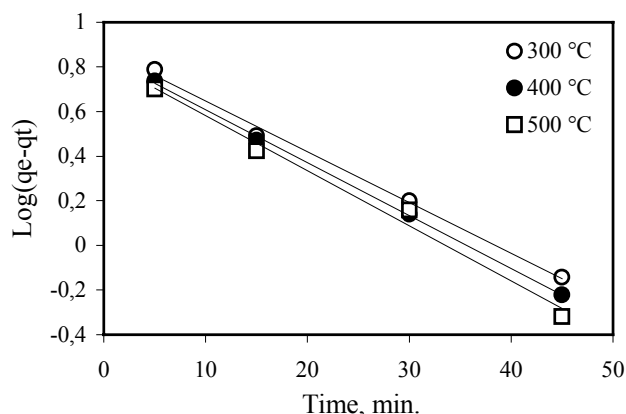
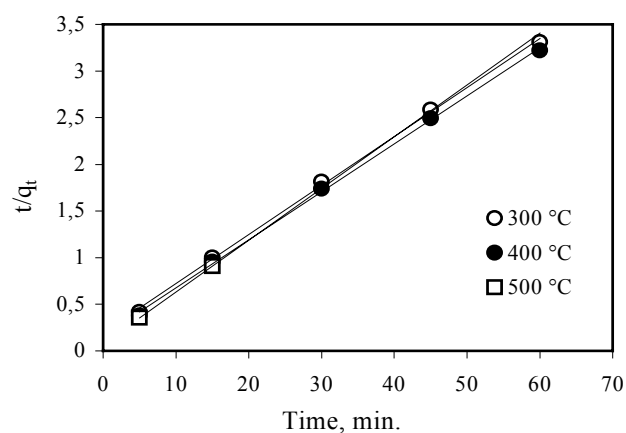
$$\log(q_e - q_t) = \log(q_e) - \frac{k}{2.303} t \quad (9)$$

and the integrated form of equation 8 for the same conditions is a linear form of second-order rate equation

$$\frac{t}{q_t} = \frac{1}{k_{2,ad}q_e^2} + \frac{1}{q_e} t \quad (10)$$

Fig. 7 shows a plot of  $\log(q_e - q_t)$  vs.  $t$  for three activated carbons at 20 °C. The first-order rate constant ( $k_{1,ad}$ ) calculated from the slope of the plots and the correlation coefficients are given in Table 5. The values of  $k_{1,ad}$  were found to be 0.0461, 0.0546 and 0.0567 l/min for activated carbon samples obtained at 300, 400 and 500 °C, respectively. Also the theoretical  $q_{ec}$  values, which should be equal to the values of  $q_e$  in ideal conditions, calculated from the intercept of plots are tabulated (Table 5). Al-

though the correlation coefficients ( $R^2$ ) determined for activated carbons obtained at different temperatures were found to be high, the difference between the values of  $q_e$  and  $q_{ec}$  did not give reasonable values. This suggests that this process do not obey well to the first-order rate expression of Lagergren.

**FIGURE 7 - Lagergren plot of Cd(II) ions adsorption by activated carbons from sugar beet pulp (Conditions: 50 ml of 100 mg/l Cd(II) solution; 0.25 g activated carbons obtained at different temperatures; initial pH 6.3; contact temperature 20 °C).****FIGURE 8 - Second-order kinetic model plot of Cd(II) ions adsorption by activated carbons from sugar beet pulp (Conditions: 50 ml of 100 mg/l Cd(II) solution; 0.25 g activated carbons obtained at different temperatures; initial pH 6.3; contact temperature 20 °C).**

**TABLE 5 - Kinetic parameters for the adsorption of Cd(II) ions on activated carbons from sugar beet pulp impregnated with phosphoric acid.**

| Carbonisation temp.<br>(°C) | First order kinetic model |       |                    |                 | Second order kinetic model |       |                    |                 |
|-----------------------------|---------------------------|-------|--------------------|-----------------|----------------------------|-------|--------------------|-----------------|
|                             | $k_{1,ad}$<br>(1/min)     | $R^2$ | $q_{ec}$<br>(mg/g) | $q_e$<br>(mg/g) | $k_{2,ad}$<br>(g/mg min)   | $R^2$ | $q_{ec}$<br>(mg/g) | $q_e$<br>(mg/g) |
| 300                         | 0.0461                    | 0.995 | 7.452              | 18.12           | 0.0141                     | 0.999 | 19.011             | 18.12           |
| 400                         | 0.0546                    | 0.999 | 6.976              | 18.64           | 0.0164                     | 0.999 | 19.417             | 18.64           |
| 500                         | 0.0567                    | 0.987 | 6.707              | 19.16           | 0.0406                     | 1.000 | 18.018             | 19.16           |

To determine the values of  $k_{2,ad}$  and  $q_{ec}$ ,  $t/q_t$  was plotted against  $t$  at 20 °C for each activated carbon (Fig. 8). The values of  $k_{2,ad}$  and  $q_{ec}$  calculated from the slope and intercept of the plots, respectively, are also presented in Table 5. The results indicated that an increase in carbonisation temperature increased the rate constant for second-order kinetic. The correlation coefficients for the second-order kinetic model are approximately equal to 1. There are no remarkable differences between the values of theoretical  $q_{ec}$  and experimental  $q_e$ , showing the best correlation of data for the second-order kinetic model and the applicability of equation 10 for the adsorption of Cd(II) ions by activated carbons.

## CONCLUSIONS

In order to examine the availability and effectiveness of activated carbon from sugar beet pulp at different temperatures for the removal of Cd(II) ions, it was observed that the removal percentage was increased with increasing contact time and reached an equilibrium state within 60 min. The optimum pH was determined as 6.3, at which the maximum removal percentages were 90.6 %, 93.4 % and 95.8 % for activated carbons obtained at 300, 400 and 500 °C, respectively.

In Cd(II) ions removal by activated carbons from sugar beet pulp, the application of Langmuir isotherm model was more appropriate than that of Freundlich. The adsorption capacities for Cd(II) of activated carbons were found to be relatively high when compared with those of many other adsorbents reported in the literature. It was noticed that the isotherm constant decreased with increasing temperature. Negative values of  $\Delta H^\circ$  indicate the exothermic nature of the adsorption process. Other thermodynamic parameters reflect the feasibility and spontaneous nature of the process using activated carbons from sugar beet pulp were used as adsorbents for Cd(II) ions removal.

The applicability of the first and second-order kinetic models for the adsorption of Cd(II) ions on activated carbons was also examined. The kinetic results showed that the adsorption of Cd(II) ions onto activated carbons fitted very well to the second-order kinetic model compared to the first-order one.

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